

# On multiphoton absorption by molecules

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(arch 17, 1998)*

Rabi frequencies for multiphoton absorption by atoms or molecules that can be characterized as two- or three-level systems are obtained in the cases of single and double laser perturbations. If the ambiguity in the origin of absolute energy is conveniently gauged off in the three-level model, there appears an additional non linear frequency which is originated from the separate evolution of a relative-frequency component induced in the whole system by the simultaneous action of the two perturbations.

Since multiphoton absorption and dissociation in small polyatomic molecules were discovered two decades ago [1,2] there has been a considerable interest [3] in the study of the mechanism by which a single monochromatic infrared laser radiation can be absorbed by a highly anharmonic molecular mode. This interest has led to a variety of models which range from those suggesting a fully stochastic interpretation [4] to models invoking rotovibrationally assisted contributions [5]. Among these models, there emerged the quite interesting possibility that intramolecular generation of deterministic chaos may become the main mechanism responsible for monochromatic multiphoton excitation of small molecules [6], with the Rabi frequency playing the role of the control parameter. Taking the Rabi frequency as a constant parameter could be not quite correct an assumption as it becomes nonlinearly dependent of radiation intensity at high intensities of the driving field [7] and therefore no longer a genuine constant of motion.

This work aims at obtaining expressions for the Rabi frequency in multiphoton processes using a fully quantized procedure when the excited molecules can be modeled as two- or three-level systems. In accordance with previous indications, it is obtained that such expressions generally depend nonlinearly on field intensity, so rendering the Rabi frequency unsuitable as constant of motion. We use two simple models. We consider first a two-level system which coherently absorb  $M$  monochromatic photons. The results from this model are compared with those obtained by other authors, and used to construct the more interesting three-level model where two independent radiation beams with different wavelengths are considered. From this we derive the main result of this work, that is the appearance of an additional nonlinear absorption frequency which can be described in terms of the relative frequency of the two driving fields. It will be seen that it is the existence of this additional frequency which distinguishes a three-level system from a two-level system with respect to multiphoton absorption.

Let us write the fully quantized Hamiltonian for the absorption of  $M$  photons with frequency  $\omega$  by the two-level system with transition frequency  $\omega_0$  in the rotating wave approximation

$$H_2 = H_R + H_M + H_{RM}$$

$$= \hbar\omega a^\dagger a + \frac{1}{2}\hbar\omega_0\sigma_z + \hbar\beta (a^{\dagger M}\sigma_- - a^M\sigma_+), \quad (1)$$

where  $a, a^\dagger$ , the annihilation and creation operators for the driving field, satisfy the usual commutation relations  $[a, a^\dagger] = 1$ , and the  $\sigma$ 's are the  $2 \times 2$  Pauli matrices which, in turn, obey the commutation relations:

$$[\sigma_z, \sigma_\pm] = \pm\sigma_\pm, \quad [\sigma_+, \sigma_-] = \sigma_z$$

$$\{\sigma_+, \sigma_-\} = I,$$

with  $I$  the unit matrix;  $\beta$  is the dipole moment matrix element for the simultaneous absorption of  $M$  monochromatic photons by the system.

The Heisenberg equations of motion read

$$\dot{\sigma}_z = 2i\beta (a^{\dagger M}\sigma_- + a^M\sigma_+)$$

$$\dot{\sigma}_+ = i(\omega_0\sigma_+ - \beta a^{\dagger M}\sigma_z) \quad (2)$$

$$\dot{a} = -i(\beta M a^{\dagger M-1}\sigma_- + \omega a).$$

Introducing the constant of motion ( $[N, H] = 0$ )

$$N = a^\dagger a + M\sigma_+\sigma_-, \quad (3)$$

we finally obtain

$$\ddot{\sigma}_z = -\frac{2(M\omega - \omega_0)}{\hbar} \left[ H_2 - \hbar\omega(N - \frac{1}{2}M) \right]$$

$$- [(M\omega - \omega_0)^2 - 2|\beta|^2 M A_2(n)] \sigma_z + [2|\beta|^2 M B_2(n)] \sigma_z^2, \quad (4)$$

where  $n = a^\dagger a$  and

$$A_2(n) = \frac{n!}{(n-M)!} + \frac{(n+M)!}{n!} \quad (5)$$

$$B_2(n) = \sum_{\alpha=0}^{M-1} \frac{(n+\alpha)!}{(n-M+\alpha+1)!}. \quad (6)$$

If we take the Rabi frequency as the coefficient of the spin operator  $\sigma_z$ , there could be some ambiguity in such a definition using expression (4) because the last term in this expression, which depends on  $\sigma_z^2$ , could either be absorbed into the definition of a unique Rabi frequency given by the coefficient of  $\sigma_z$  (notice that the insertion of  $\sigma_z = 2\sigma_+\sigma_- - 1$  in the last term of (4) allows one to factorize a given coefficient for  $\sigma_z$  depending on  $\sigma_+\sigma_-$  in that term, and then by using (3), one may rearrange that coefficient, together with the similar one in the second term, in such a way that the resulting overall coefficient for  $\sigma_z$  will not explicitly depend on operators  $\sigma_+\sigma_-$  and  $\sigma_z$ , but on  $N$  and  $n$ ), or define by itself a new nonlinear fundamental frequency if we would interpret this as the coefficient of the spin operator squared  $\sigma_z^2$ . For the case of a two-level system only the first possibility applies because, once the physically irrelevant energy-origin gauge is subtracted off, we are left with just one single periodic evolution for the two eigenstates in the semiclassical treatment; i.e.: for two-level systems, one can always have an one-body representation of the pure molecular Hamiltonian and this should associate with a single Rabi frequency given by

$$\Omega_R^2 = (M\omega - \omega_0)^2$$

$$+ 2|\beta|^2 [MA_2(n) - B_2(n)(M - 2N + 2n)]. \quad (7)$$

Thus,  $\Omega_R$  is no longer a constant of motion and depends explicitly on  $n$  nonlinearly for  $M > 1$ . Similar expressions have been obtained by Sukumar and Buck [8] and Kochetov [9]. We note that expression (7) reduces to the known Knight-Milonni equation [10] for the case of linear absorption  $M = 1$ .

The existence of only a single linear Rabi frequency,  $\Omega_R$ , is no longer a characteristic of multiphoton absorption by a  $N$ -level system when  $N > 2$ . In dealing with the molecular Hamiltonian as a level system in terms of the absolute energies of the levels, one always has an ambiguity in the choice of the origin for such energies. This ambiguity is eliminated by re-expressing the Hamiltonian in terms of the level transition energies rather than absolute energies. In the case of a three-level system,  $N=3$ , this can be done by writing  $H_M$  as (Fig. 1)

$$H_M = \frac{1}{2} \{ (E_1 + E_3)I + (E_3 - E_1)S + [2E_2 - (E_1 + E_3)] S_5 \} [n_2, H_3] = 0 \quad (8)$$

where

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (9)$$

and

$$S_5 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (10)$$

Then, since  $S_5 = I - S^2$ , (8) transforms into:

$$H_M = E_2 I + \frac{1}{2} \hbar(\omega_0 + \omega_1)S - \frac{1}{2} \hbar(\omega_0 - \omega - 1)S^2. \quad (11)$$

The matrix  $I$  can be dropped off from (11) by a convenient shift of the energy origin. Taking this origin at the energy of the intermediate level  $E_2$ , we have

$$H_M = \frac{1}{2} \hbar(\omega_0 + \omega_1)S - \frac{1}{2} \hbar(\omega_0 - \omega - 1)S^2. \quad (12)$$

Thus, much as it is usually done in the two-body problem of mechanics, we have reduced the three level problem to the separate evolution of the center of energies and the relative energy. Note that for the harmonic-oscillator case only the term depending on  $(\omega_0 + \omega_1)$  survives. When  $\omega_0 \neq \omega_1$  there would then be an additional radiative mechanism to be superimposed to the usual one. Hence, two independent contributing frequencies should be expected.

The fully quantized Hamiltonian for the three-level molecular system depicted in Fig. 1, for the case that we irradiate with two beams of frequencies  $\omega_{L1}$  and  $\omega_{L2}$  becomes

$$H_3 = \hbar\omega_{L1}a_1^\dagger a_1 + \hbar\omega_{L2}a_2^\dagger a_2$$

$$+ \frac{1}{2} \hbar [(\omega_0 + \omega_1)S - (\omega_0 - \omega_1)S^2$$

$$+ 2\beta \left( a_1^{\dagger M} a_2^{\dagger(N-M)} S_8 S_4 - a_1^M a_2^{(N-m)} S_2 S_6 \right)], \quad (13)$$

where  $\beta$  is now the dipole moment matrix element for the total absorption of the  $N$  photons,  $M$  with energy  $\hbar\omega_{L1}$  and  $N - M$  with energy  $\hbar\omega_{L2}$ . The operators  $S_i$  are the generators of the unitary group  $U(3)$  and obey

$$[S_i, S_j] = C_{ij}^k S_k, \quad (14)$$

in which  $i, j, k = 1, 2, \dots, 9$ , and  $C_{ij}^k$  are the structure constants.

Introducing the constants of motion  $([N_1, H_3] =$

$$N_1 = a_1^\dagger a_1 + \frac{M}{2} S$$

$$N_2 = a_2^\dagger a_2 + \frac{n-M}{2} S, \quad (15)$$

from the Heisenberg equations, we obtain finally

$$\ddot{S} = \frac{\epsilon}{\hbar}(H_3 - \hbar\omega_{L1}N_1 - \hbar\omega_{L2}N_2)\Omega_{Rc}^2S + \Omega_{Rr}^2S^2, \quad (16)$$

where

$$\epsilon = 2[\omega_0 + \omega_1 - M\omega_{L1} - (N - M)\omega_{L2}]$$

$$\begin{aligned} \Omega_{Rc}^2 &= -\frac{\epsilon}{2}(\omega_0 + \omega_1 - M\omega_{L1}) \\ &+ \frac{\epsilon}{2}(N - M)\omega_{L2} - |\beta|^2 A_3(n_1, n_2) \end{aligned} \quad (17)$$

$$\Omega_{Rr}^2 = -\frac{\epsilon}{2}(\omega_1 - \omega_0) - 2|\beta|^2 B_3(n_1, n_2) \quad (18)$$

with

$$\begin{aligned} A_3(n_1, n_2) &= \frac{n_1!n_2!}{(n_1 - M)!(n_2 - N + M)!} \\ &+ \frac{(n_1 + M)!(n_2 + N - M)!}{n_1!n_2!}, \end{aligned}$$

$$\begin{aligned} B_3(n_1, n_2) &= M \frac{n_2!}{(n_2 - N + M)!} \sum_{\alpha=0}^{M-1} \frac{(n_1 + \alpha)!}{(n_1 - M + \alpha + 1)!} \\ &+ (N - M) \frac{n_1!}{(n_1 - M)!} \sum_{\gamma=0}^{N-M-1} \frac{(n_2 + \gamma)!}{(n_2 - N + M + \gamma + 1)!}, \end{aligned}$$

and  $n_i = a_i^\dagger a_i$ .

The roots of the coefficients for the matrices  $S$  and  $S^2$  can be consistently interpreted, respectively, as the Rabi frequency for the center of energies  $\Omega_{Rc}$ , and the Rabi frequency for the relative energy  $\Omega_{Rr}$ . We see that (15) and (16) are again radiation-intensity dependent.

For  $N = M = 1$  in the limit  $\omega_1 = \omega_{L1} \rightarrow 0$ ,  $S \rightarrow \sigma_z$  and  $\beta \rightarrow f$ , so that the whole three-level system reduces to an *effective* two-level system, and  $\Omega_{Rr}$  becomes a constant to be absorbed, one part,  $-2|f|^2$ , into the conventional Rabi frequency, and the other part,  $\omega_0(\omega_0 - \omega_{L1})$ , into the counter-part of the first term in the r.h.s. of (14) which contains the constants of motion. This seems to suggest that  $\Omega_{Rr}$  ultimately originates from a nonlinear contribution to radiation-matter interaction through which both radiation beams and the matter system would all cooperate. In fact, the only contributions that can survive the rotating wave approximation with respect to  $\omega_0 - \omega_1$  in the semiclassical treatment (where we consider a quantized matter system being perturbed by a classical radiation field [11]) are those arising from nonlinear terms which simultaneously contain both radiation field perturbations. Thus, one should regard the presence of the separately-operating frequencies  $\Omega_{Rc}$  and  $\Omega_{Rr}$  as a consequence from the full-quantized picture. In the

semiclassical treatment, possible somewhat analogous effects arising from the novel non-linear Rabi frequency could still be found, though they would not be expected to be visualizable as being driven from two independent Rabi frequencies, but rather from a more complicate single Rabi parameter.

The incidence that one could expect from the above predictions on multiphoton absorption of polyatomic molecules is twofold. On one hand, the new Rabi frequency would provide us with a novel mechanism to help overcoming the molecular anharmonic barrier operating in the few low-lying levels; on the other hand, such a Rabi frequency would play the role of still another control parameter in models where dichromatic multiphoton excitation is assumed to be driven by intermolecular generation of deterministic chaos, allowing for a more effective coupling of the active excited levels to a harmonic reservoir, and hence leading to an increase of the multiphoton absorption cross section.

In summary, starting with the consideration of multiphoton absorption by a two-level system, the present report contains the derivation of two fundamental frequencies in order to characterize a two-frequency laser induced multiabsorption by a three-level system. Such frequencies are radiation-intensity dependent and correspond to the center of energy and relative energy, respectively.

## ACKNOWLEDGMENTS

For helpful comments and help in the calculations, the author thanks C. Sigenza and M. Santos. This research was supported by DGICYT under research projects N PB94-0107 and N PB93-0139.

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### Legend for Figures

- Fig. 1. Relevant transitions in a three-level system.